United States
Environmental Protection
Agency

Office of Research and
Development
Washington DC 20460

EPA/600/R-98/128
September 1998

EPA

Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water

TECHNICAL PROTOCOL FOR EVALUATING NATURAL ATTENUATION OF CHLORINATED SOLVENTS IN GROUND WATER

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NOTICE

The information in this document was developed through a collaboration between the U.S. EPA (Subsurface Protection and Remediation Division, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, Oklahoma [SPRD]) and the U.S. Air Force (U.S. Air Force Center for Environmental Excellence, Brooks Air Force Base, Texas [AFCEE]). EPA staff were primarily responsible for development of the conceptual framework for the approach presented in this document; staff of the U.S. Air Force and their contractors also provided substantive input. The U.S. Air Force was primarily responsible for field testing the approach presented in this document. Through a contract with Parsons Engineering Science, Inc., the U.S. Air Force applied the approach at chlorinated solvent plumes at a number of U.S. Air Force Bases. EPA staff conducted field sampling and analysis with support from ManTech Environmental Research Services Corp., the in-house analytical support contractor for SPRD.

All data generated by EPA staff or by ManTech Environmental Research Services Corp. were collected following procedures described in the field sampling Quality Assurance Plan for an in-house research project on natural attenuation, and the analytical Quality Assurance Plan for ManTech Environmental Research Services Corp.

This protocol has undergone extensive external and internal peer and administrative review by the U.S. EPA and the U.S. Air Force. This EPA Report provides technical recommendations, not policy guidance. It is not issued as an EPA Directive, and the recommendations of this EPA Report are not binding on enforcement actions carried out by the U.S. EPA or by the individual States of the United States of America. Neither the United States Government (U.S. EPA or U.S. Air Force), Parsons Engineering Science, Inc., or any of the authors or reviewers accept any liability or responsibility resulting from the use of this document. Implementation of the recommendations of the document, and the interpretation of the results provided through that implementation, are the sole responsibility of the user.

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet these mandates, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The focus of the Laboratory's research program is on methods for the prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites and ground water; and prevention and control of indoor air pollution. The goal of this research effort is to catalyze development and implementation of innovative, cost-effective environmental technologies; develop scientific and engineering information needed by EPA to support regulatory and policy decisions; and provide technical support and information transfer to ensure effective implementation of environmental regulations and strategies.

The site characterization processes applied in the past are frequently inadequate to allow an objective and robust evaluation of natural attenuation. Before natural attenuation can be used in the remedy for contamination of ground water by chlorinated solvents, additional information is required on the three-dimensional flow field of contaminated ground water in the aquifer, and on the physical, chemical and biological processes that attenuate concentrations of the contaminants of concern. This document identifies parameters that are useful in the evaluation of natural attenuation of chlorinated solvents, and provides recommendations to analyze and interpret the data collected from the site characterization process. It will also allow ground-water remediation managers to incorporate natural attenuation into an integrated approach to remediation that includes an active remedy, as appropriate, as well as natural attenuation.

Clinton W. Hall, Director
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ACKNOWLEDGMENTS

The authors would like to thank Dr. Robert Hinchee, Doug Downey, and Dr. Guy Sewell for their contributions and their extensive and helpful reviews of this manuscript. Thanks also to Leigh Alvarado Benson, R. Todd Herrington, Robert Nagel, Cindy Merrill, Peter Guest, Mark Vesseley, John Hicks, and Saskia Hoffer for their contributions to this project.

LIST OF ACRONYMS AND ABBREVIATIONS

AAR	American Association of Railroads
AFB	Air Force Base
AFCEE	Air Force Center for Environmental Excellence
ASTM	American Society for Testing and Materials
bgs	below ground surface
BRA	baseline risk assessment
BRAC	Base Realignment and Closure
BTEX	benzene, toluene, ethylbenzene, xylenes
CAP	corrective action plan
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
cfm	cubic feet per minute
CFR	Code of Federal Regulations
COPC	chemical of potential concern
CPT	cone penetrometer testing
CSM	conceptual site model
DAF	dilution/attenuation factor
DERP	Defense Environmental Restoration Program
DNAPL	Dense Nonaqueous Phase Liquid
DO	dissolved oxygen
DOD	Department of Defense
DQO	data quality objective
EE/CA	engineering evaluation/cost analysis
FS	feasibility study
gpd	gallons per day
G_r	standard (Gibbs) free energy
HDPE	high-density polyethylene
HSSM	Hydrocarbon Spill Screening Model
HSWA	Hazardous and Solid Waste Amendments of 1984
ID	inside-diameter
IDW	investigation derived waste
IRP	Installation Restoration Program
L	liter
LEL	lower explosive limit
LNAPL	light nonaqueous-phase liquid
LUFT	leaking underground fuel tank
MAP	management action plan
MCL	maximum contaminant level

MDL	method detection limit
µg	microgram
µg/kg	microgram per kilogram
µg/L	microgram per liter
mg	milligram
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
mg/m^3	milligrams per cubic meter
mm Hg	millimeters of mercury
MOC	method of characteristics
MOGAS	motor gasoline
NAPL	nonaqueous-phase liquid
NCP	National Contingency Plan
NFRAP	no further response action plan
NOAA	National Oceanographic and Atmospheric Administration
NOEL	no-observed-effect level
NPL	National Priorities List
OD	outside-diameter
ORP	oxidation-reduction potential
OSHA	Occupational Safety and Health Administration
OSWER	Office of Solid Waste and Emergency Response
PAH	polycyclic aromatic hydrocarbon
PEL	permissible exposure limit
POA	point-of-action
POC	point-of-compliance
POL	petroleum, oil, and lubricant
ppmv	parts per million per volume
psi	pounds per square inch
PVC	polyvinyl chloride
QA	quality assurance
QC	quality control
RAP	remedial action plan
RBCA	risk-based corrective action
RBSL	risk-based screening level
redox	reduction/oxidation
RFI	RCRA facility investigation
RI	remedial investigation
RME	reasonable maximum exposure
RPM	remedial project manager
SAP	sampling and analysis plan
SARA	Superfund Amendments and Reauthorization Act
scfm	standard cubic feet per minute
SPCC	spill prevention, control, and countermeasures

SSL	soil screening level
SSTL	site-specific target level
SVE	soil vapor extraction
SVOC	semivolatile organic compound
TC	toxicity characteristic
TCLP	toxicity-characteristic leaching procedure
TI	technical impracticability
TMB	trimethylbenzene
TOC	total organic carbon
TPH	total petroleum hydrocarbons
TRPH	total recoverable petroleum hydrocarbons
TVH	total volatile hydrocarbons
TVPH	total volatile petroleum hydrocarbons
TWA	time-weighted-average
UCL	upper confidence limit
US	United States
USGS	US Geological Survey
UST	underground storage tank
VOCs	volatile organic compounds

DEFINITIONS

Aerobe: bacteria that use oxygen as an electron acceptor.

Anabolism: The process whereby energy is used to build organic compounds such as enzymes and nucleic acids that are necessary for life functions. In essence, energy is derived from catabolism, stored in high-energy intermediate compounds such as adenosine triphosphate (ATP), guanosine triphosphate (GTP) and acetyl-coenzyme A, and used in anabolic reactions that allow a cell to grow.

Anaerobe: Organisms that do not require oxygen to live.

Area of Attainment: The area over which cleanup levels will be achieved in the ground water. It encompasses the area outside the boundary of any waste remaining in place and up to the boundary of the contaminant plume. Usually, the boundary of the waste is defined by the source control remedy. Note: this area is independent of property boundaries or potential receptors - it is the plume area which the ground water must be returned to beneficial use during the implementation of a remedy.

Anthropogenic: Man-made.

Autotrophs: Microorganisms that synthesize organic materials from carbon dioxide.

Catabolism: The process whereby energy is extracted from organic compounds by breaking them down into their component parts.

Coefficient of Variation: Sample standard deviation divided by the mean.

Cofactor: A small molecule required for the function of an enzyme.

Cometabolism: The process in which a compound is fortuitously degraded by an enzyme or cofactor produced during microbial metabolism of another compound.

Daughter Product: A compound that results directly from the biodegradation of another. For example *cis*-1,2-dichloroethene (*cis*-1,2-DCE)is commonly a daughter product of trichloroethene (TCE).

Dehydrohalogenation: Elimination of a hydrogen ion and a halide ion resulting in the formation of an alkene.

Diffusion: The process whereby molecules move from a region of higher concentration to a region of lower concentration as a result of Brownian motion.

Dihaloelimination: Reductive elimination of two halide substituents resulting in formation of an alkene.

Dispersivity: A property that quantifies mechanical dispersion in a medium.

Effective Porosity: The percentage of void volume that contributes to percolation; roughly equivalent to the specific yield.

Electron Acceptor: A compound capable of accepting electrons during oxidation-reduction reactions. Microorganisms obtain energy by transferring electrons from electron donors such as organic compounds (or sometimes reduced inorganic compounds such as sulfide) to an electron acceptor. Electron acceptors are compounds that are relatively oxidized and include oxygen, nitrate, iron (III), manganese (IV), sulfate, carbon dioxide, or in some cases the chlorinated aliphatic hydrocarbons such as perchloroethene (PCE), TCE, DCE, and vinyl chloride.

Electron Donor: A compound capable of supplying (giving up) electrons during oxidation-reduction reactions. Microorganisms obtain energy by transferring electrons from electron donors such as organic compounds (or sometimes reduced inorganic compounds such as sulfide) to an electron acceptor. Electron donors are compounds that are relatively reduced and include fuel hydrocarbons and native organic carbon.

Electrophile: A reactive species that accepts an electron pair.

Elimination: Reaction where two groups such as chlorine and hydrogen are lost from adjacent carbon atoms and a double bond is formed in their place.

Epoxidation: A reaction wherein an oxygen molecule is inserted in a carbon-carbon double bond and an epoxide is formed.

Facultative Anaerobes: microorganisms that use (and prefer) oxygen when it is available, but can also use alternate electron acceptors such as nitrate under anaerobic conditions when necessary.

Fermentation: Microbial metabolism in which a particular compound is used both as an electron donor and an electron acceptor resulting in the production of oxidized and reduced daughter products.

Heterotroph: Organism that uses organic carbon as an external energy source and as a carbon source.

Hydraulic Conductivity: The relative ability of a unit cube of soil, sediment, or rock to transmit water.

Hydraulic Head: The height above a datum plane of the surface of a column of water. In the groundwater environment, it is composed dominantly of elevation head and pressure head.

Hydraulic Gradient: The maximum change in head per unit distance.

Hydrogenolysis: A reductive reaction in which a carbon-halogen bond is broken, and hydrogen replaces the halogen substituent.

Hydroxylation: Addition of a hydroxyl group to a chlorinated aliphatic hydrocarbon.

Lithotroph: Organism that uses inorganic carbon such as carbon dioxide or bicarbonate as a carbon source and an external source of energy.

Mechanical Dispersion: A physical process of mixing along a flow path in an aquifer resulting from differences in path length and flow velocity. This is in contrast to mixing due to diffusion.

Metabolic Byproduct: A product of the reaction between an electron donor and an electron acceptor. Metabolic byproducts include volatile fatty acids, daughter products of chlorinated aliphatic hydrocarbons, methane, and chloride.

Monooxygenase: A microbial enzyme that catalyzes reactions in which one atom of the oxygen molecule is incorporated into a product and the other atom appears in water.

Nucleophile: A chemical reagent that reacts by forming covalent bonds with electronegative atoms and compounds.

Obligate Aerobe: Microorganisms that can use only oxygen as an electron acceptor. Thus, the presence of molecular oxygen is a requirement for these microbes.

Obligate Anaerobes: Microorganisms that grow only in the absence of oxygen; the presence of molecular oxygen either inhibits growth or kills the organism. For example, methanogens are very sensitive to oxygen and can live only under strictly anaerobic conditions. Sulfate reducers, on the other hand, can tolerate exposure to oxygen, but cannot grow in its presence (Chapelle, 1993).

Performance Evaluation Well: A ground-water monitoring well placed to monitor the effectiveness of the chosen remedial action.

Porosity: The ratio of void volume to total volume of a rock or sediment.

Respiration: The process of coupling oxidation of organic compounds with the reduction of inorganic compounds, such as oxygen, nitrate, iron (III), manganese (IV), and sulfate.

Solvolysis: A reaction in which the solvent serves as the nucleophile.

Table i: Contaminants with Federal Regulatory Standards Considered in this Document

Abbreviation	Chemical Abstracts Service (CAS) Name	CAS Number	Other Names	Molecular Formula
PCE	tetrachloroethene	127-18-4	perchloroethylene; tetrachloroethylene	C_2Cl_4
TCE	trichloroethene	79-01-6	trichloroethylene	C_2HCl_3
1,1-DCE	1,1-dichloroethene	75-35-4	1,1-dichloroethylene; vinylidine chloride	$C_2H_2Cl_2$
trans-1,2-DCE	(E)-1,2-dichloroethene	156-60-5	trans-1,2-dichloroethene;trans-1,2- dichloroethylene	$C_2H_2Cl_2$
cis-1,2-DCE		156-59-2	cis-1,2-dichloroethene; cis-1,2-dichloroethylene	$C_2H_2Cl_2$
VC	chloroethene	75-01-4	vinyl chloride; chloroethylene	C_2H_3Cl
1,1,1-TCA	1,1,1-trichloroethane	71-55-6		$C_2H_3Cl_3$
1,1,2-TCA	1,1,2-trichloroethane	79-00-5		$C_2H_3Cl_3$
1,1-DCA	1,1-dichloroethane	75-34-3		$C_2H_4Cl_2$
1,2-DCA	1,2-dichloroethane	107-06-02		$C_2H_4Cl_2$
CA	chloroethane	75-00-3		C_2H_5Cl
CF	trichloromethane	67-66-3	chloroform	$CHCl_3$
CT	tetrachloromethane	56-23-5	carbon tetrachloride	CCl_4
Methylene Chloride	dichloromethane	75-09-2	methylene dichloride	CH_2Cl_2
CB	chlorobenzene	108-90-7		C_6H_5Cl
1,2-DCB	1,2-dichlorobenzene	95-50-1	o-dichlorobenzene	$C_6H_4Cl_2$
1,3-DCB	1,3-dichlorobenzene	541-73-1	m-dichlorobenzene	$C_6H_4Cl_2$
1,4-DCB	1,4-dichlorobenzene	106-46-7	p-dichlorobenzene	$C_6H_4Cl_2$
1,2,3-TCB	1,2,3-trichlorobenzene	87-61-6		$C_6H_3Cl_3$
1,2,4-TCB	1,2,4-trichlorobenzene	120-82-1		$C_6H_3Cl_3$
1,3,5-TCB	1,3,5-trichlorobenzene	108-70-3		$C_6H_3Cl_3$
1,2,3,5-TECB	1,2,3,5-tetrachlorobenzene	634-90-2	1,2,3,5-TCB	$C_6H_2Cl_4$
1,2,4,5-TECB	1,2,4,5-tetrachlorobenzene	95-94-3		$C_6H_2Cl_4$
HCB	hexachlorobenzene	118-74-1		C_6Cl_6
EDB	1,2-dibromoethane	106-93-4	ethylene dibromide; dibromoethane	$C_2H_4Br_2$